

# Superconductivity and Magnetic Properties of high-quality single crystals of $A_x\text{Fe}_2\text{Se}_2$ ( $A = \text{K}$ and $\text{Cs}$ )

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We successfully grew the high-quality single crystals of  $A_x\text{Fe}_2\text{Se}_2$  ( $A = \text{K}$  and  $\text{Cs}$ ) by self-flux method. Sharp superconducting transition was observed for both types of crystals. The crystals show the onset superconducting transition temperatures ( $T_c$ ) of 31 K and 30 K for K- and Cs-compounds, respectively, with nearly 100% shielding fraction. The crystals show quite high resistivity in the normal state of more than 160 mΩ cm and 1300 mΩ cm maximum resistivity for  $\text{K}_{0.86}\text{Fe}_2\text{Se}_{1.82}$  and  $\text{Cs}_{0.86}\text{Fe}_{1.66}\text{Se}_2$  single crystals, respectively. Much larger upper critical field  $H_{c2}$  is inferred from low-temperature iso-magnetic-field magnetoresistance in these crystals than in FeSe. The anisotropy  $H_{c2}^{ab}(0)/H_{c2}^c(0)$  is around 3 for both of the two materials. Anisotropic peculiar magnetic behavior in normal state has been found for  $\text{Cs}_{0.86}\text{Fe}_{1.66}\text{Se}_2$

The layered iron-pnictide compounds have attracted the intense interests since superconductivity at 26 K in ZrCuSiAs-type  $\text{LaFeAs}(\text{O},\text{F})$  [1] was found. Replacement La with Sm leads to superconducting transition temperature  $T_c = 43$  K [2] and soon renewed to highest record ( $T_c = 55$  K) [3, 4] in this type of compound. Up to now, various Fe-based superconductors, such as ZrCuSiAs-type  $\text{LnFeAsO}$  ( $\text{Ln}$  is rare earth elements) [1–3],  $\text{ThCr}_2\text{Si}_2$ -type  $\text{AeFe}_2\text{As}_2$  ( $\text{Ae}$  is alkali earth elements) [6],  $\text{Fe}_2\text{As}$ -type  $\text{AFeAs}$  ( $A$  is Li or Na) [9–11] and anti-PbO-type  $\text{Fe}(\text{Se},\text{Te})$  [8], have been reported. The high  $T_c$  and superconductivity proximity to a magnetically ordering state [7, 12], which is thought to be similar to high- $T_c$  superconductor cuprates, inspired worldwide passion of study towards elucidating the mechanism of high- $T_c$  superconductivity. All of them have a common structural feature, that is, the edge-sharing  $\text{FeAs}_4$  ( $\text{FeSe}_4$ ) tetrahedra formed  $\text{FeAs}$  ( $\text{FeSe}$ ) layers. The superconductivity in these compounds is thought to be intimately related to the height of anion from Fe layer [13]. Unlike the case of  $\text{FeAs}$ -based compounds, which usually possess cations between the  $\text{FeAs}$  layers,  $\text{Fe}(\text{Se},\text{Te})$  family has a extremely simple structure with only  $\text{FeSe}$  layers stacked along  $c$ -axis without any intercalating cations. [8] To tune the height of anion from Fe layer in  $\text{Fe}(\text{Se},\text{Te})$  can only be realized by changing the relative proportion of Se and Te anions or by applying high pressure.  $T_c$  can reach 37 K (onset) under 4.5 GPa from the ambient 8 K in  $\text{FeSe}$ . [14] The corresponding pressure dependent ratio of  $T_c$  can reach as large as  $dT_c/dP$  of  $\sim 9.1$  K/GPa, which is the highest among all the Fe-base superconductors. [14] Taking into account the effect of local structure on superconductivity in the  $\text{FeAs}$ -based compounds, superconductivity in  $\text{Fe-Se}$  family is expected to have a higher  $T_c$  at ambient pressure by intercalating cations into be-

tween the  $\text{FeSe}$  layers. Very recently, by intercalating K and Cs into between the  $\text{FeSe}$  layers, superconductivity has been enhanced to be 30 K and 27 K (onset temperature) without any external pressure in  $\text{Fe-Se}$  system. [15–17] Although the highest  $T_c$  at ambient pressure for Fe-chalcogenides was achieved in K-intercalated  $\text{FeSe}$ , the superconducting fraction is low and the transition is broad. No full shielding fraction can be observed in Cs-intercalated  $\text{FeSe}$  samples either. Therefore, to investigate further intrinsic properties of intercalated  $\text{FeSe}$  compounds, single crystals with high quality with full shielding fraction and sharp transition are required to grow in priority.

In this report, we successfully grew the single crystals of  $\text{K}_x\text{Fe}_2\text{Se}_2$  and  $\text{Cs}_x\text{Fe}_2\text{Se}_2$  with full shielding fraction by self-flux method. The crystals showed the onset  $T_c$  of 31 K and 30 K for K- and Cs-compounds, respectively. Nearly 100% superconducting volume fraction was observed through the zero-field-cooling (ZFC) magnetic susceptibility measurements. Since Fe-base high- $T_c$  superconductors are thought to be related to magnetic interaction closely, the normal-state magnetization was also investigated.

Single crystals  $\text{AFe}_2\text{Se}_2$  ( $A = \text{K}, \text{Cs}$ ) were grown by self-flux method. Starting material  $\text{FeSe}$  was obtained by reacting Fe powder with Se powder with Fe: Se = 1: 1 at 700 °C for 4 hours. K and Cs pieces and  $\text{FeSe}$  powder were put into a small quartz tube with nominal composition as  $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$  and  $\text{Cs}_{0.8}\text{Fe}_2\text{Se}_2$ . Due to the high activity of K and Cs metal, the single wall quartz tube will be corrupted and broken during the growth procedure. Therefore, two wall quartz tube is required. We realized it in the following way: the small quartz tube was sealed under high vacuum and then was put in a bigger quartz tube following by evacuating and being sealed. The mixture was heated to 1030 °C in 4 hours and then kept at this temperature for 2 hours, and later slowly cooled down to 750 °C with 6 °C/ hours. After that, the temperature was cooled down to room temperature by shutting down the furnace. The obtained single crystals

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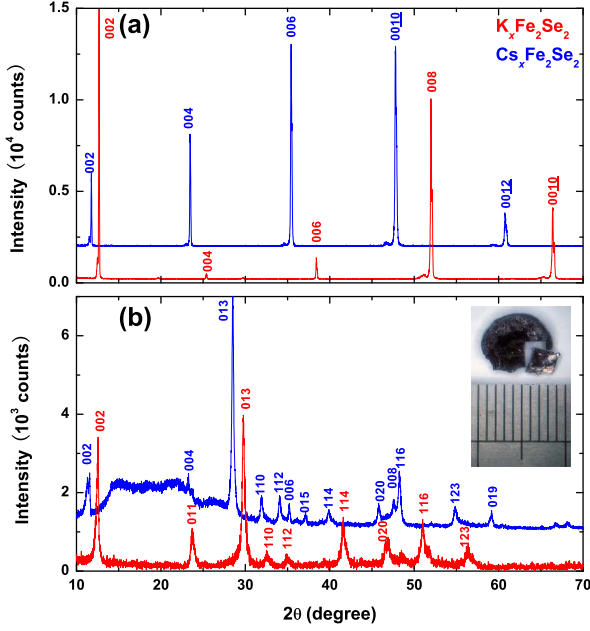


FIG. 1: (Color online) (a): The single crystal x-ray diffraction pattern of  $K_xFe_2Se_2$  (red line) and  $Cs_xFe_2Se_2$  (blue line); (b): X-ray diffraction pattern of the powdered  $K_xFe_2Se_2$  (red) and  $Cs_xFe_2Se_2$  (blue line), all the peaks can be well indexed. The hump in XRD pattern for  $Cs_xFe_2Se_2$  comes from the Mylar film, which has been used to protect the sample from air.

show the flat shiny surface with dark black color. The inset of Fig.1b shows a piece of typical single crystal of  $Cs_xFe_2Se_2$ . For K-compound crystals are easy to cleave and thin crystals with thickness less than 100  $\mu m$  can be easily obtained, while for Cs-compound crystals are fragile and quite difficult to cleave.

Single crystals of  $K_xFe_2Se_2$  and  $Cs_xFe_2Se_2$  were characterized by powder X-ray diffraction (XRD), and X-ray single crystal diffraction, and Energy dispersive X-ray (EDX) spectroscopy, and direct current (dc) magnetic susceptibility, and electrical transport measurements. Powder XRD and single crystal XRD were performed on TTRAX3 theta/theta rotating anode X-ray Diffractometer (Japan) with Cu  $K\alpha$  radiation and a fixed graphite monochromator. Magnetic susceptibility is measured with the *Quantum Design* MPMS-SQUID. The measurement of resistivity and magnetoresistance were performed using the *Quantum Design* PPMS-9.

Figure 1 shows the X-ray single crystal diffraction and powder XRD after crushing the single crystals to powder for  $K_xFe_2Se_2$  and  $Cs_xFe_2Se_2$ . Only (00 $l$ ) reflections were recognized in Fig. 1a, indicating that both types of single crystals were perfectly oriented along  $c$ -axis. The lattice parameters are obtained to index the powder XRD patterns in Fig. 1b with the symmetry of  $I4/mmm$  and  $a = 3.8912$   $\text{\AA}$  and  $c = 14.1390$   $\text{\AA}$  for  $K_xFe_2Se_2$ . The lattice constant  $a$  obtained here is smaller than that in Refs.14, 15 and 16. The actual compositions of  $K_{0.86}Fe_2Se_{1.82}$

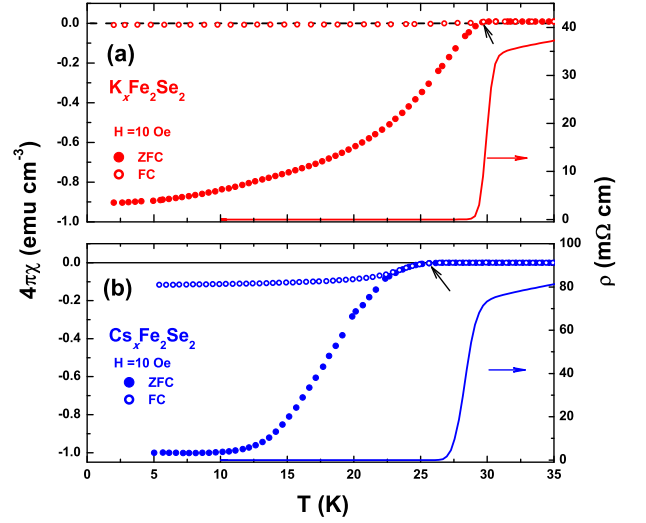


FIG. 2: (Color online) (a): The resistivity of  $K_{0.86}Fe_2Se_{1.82}$  around  $T_c$  (red solid line), and its ZFC and FC susceptibility taken at 10 Oe with the magnetic field parallel to the  $ab$ -plane. (b): The resistivity of  $Cs_{0.86}Fe_{1.66}Se_2$  around  $T_c$  (blue solid line), and its ZFC and FC susceptibility taken at 10 Oe with the magnetic field parallel to the  $ab$ -plane.

were determined by EDX using an average of different 6 points, indicating the existence of K and Se deficiencies. This is different from previous reports, where K and Fe sites show deficiencies.[15–17] For  $Cs_xFe_2Se_2$ , the lattice parameters determined from the powder XRD patterns are  $a = 3.9618$   $\text{\AA}$  and  $c = 15.285$   $\text{\AA}$ , which is almost the same as that in Ref. 16. The actual composition of  $Cs_{0.86}Fe_{1.66}Se_2$  were determined by an average of 6 different points EDX measurements, indicative of deficiencies on both Cs and Fe sites. This is consistent with previous reports.[16, 17]

Figure 2a shows the resistivity and susceptibility measurements at low temperature for  $K_{0.86}Fe_2Se_{1.82}$ . The resistivity starts to drop quickly at about 31 K and it reaches zero at about 28.7 K. The ZFC and field cooling (FC) susceptibilities show that the superconducting shield begins to emerge at about 29 K with magnetic field parallel to the  $ab$ -plane taken at 10 Oe. The superconducting volume fraction estimated from the ZFC magnetization at 2 K is about 90%, which indicates the bulk superconductivity nature and good quality of the crystals. This superconducting fraction is much larger than that in previous reports.[15–17] Fig.2b shows the low-temperature resistivity and susceptibility measurements for  $Cs_{0.86}Fe_{1.66}Se_2$ . The onset transition temperature is about 30 K, and zero resistance is reached at 26.5 K. The superconductivity transition temperature taken from the ZFC and FC curves is estimated about 25.5 K. The superconducting volume fraction estimated from the ZFC magnetization reaches 100% below 10 K estimated from the ZFC curve. It indicates a much better superconductivity than the crystals in the previous report.[17]

The temperature dependence of in-plane resistivity for

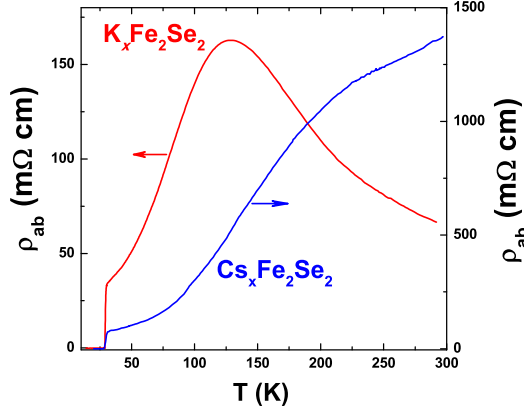


FIG. 3: (Color online) The temperature dependence of resistivity for  $K_{0.86}Fe_2Se_{1.82}$  (red line) and  $Cs_{0.86}Fe_{1.66}Se_2$  (blue line).

the  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$  from 10 to 300 K. The  $K_{0.86}Fe_2Se_{1.82}$  crystal shows the semiconducting behavior at the high temperature and displays a broad maximum at about 125 K. This temperature is slight higher than that in the report by Guo *et al.* (around 100 K) [15], but much smaller than that reported by Mizuguchi *et al.* ( $\sim 200$  K). [16] Also, the maximum resistivity in our sample (170 mΩ cm) is much smaller than that in previous report ( $\sim 3000$  mΩ cm). [16] The temperature and magnitude of the maximum resistivity could be related to the deficiency of Fe or Se, and large Fe deficiencies have been reported by early authors. [15, 16] With further decreasing the temperature, the resistivity exhibits a metallic behavior and superconductivity emerges at about 30 K. The resistivity of  $Cs_{0.86}Fe_{1.66}Se_2$  shows a metallic behavior in the whole measuring temperature range, being quite different from that of the  $K_{0.86}Fe_2Se_{1.82}$ . The resistivity of  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$  are 70 mΩ cm and 1350 mΩ cm at room temperature, respectively, and all these values are much larger than those of FeSe single crystals [18] and the iron-pnictide superconductors [19]. This may arise from the strong scattering from large disorder induced by the Fe or Se deficiencies.

The resistivity of  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$  with the different magnitude of magnet field applied parallel and perpendicular to the  $ab$ -plane around  $T_c$  are shown in Fig. 5a, b, c and d, respectively. The transition temperature of superconductivity is suppressed gradually and the transition is broadened with increasing the magnetic field. We defined the  $T_c$  as the temperature where the resistivity was 90%, 50% and 10% drop above the superconducting transition. The anisotropy of the  $H_{c2}(T)$  for  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$  is shown in Fig 5. (e) and (f), respectively. Within the weak-coupling BCS theory, the upper critical field at  $T=0$  K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation [20]  $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$ . Using

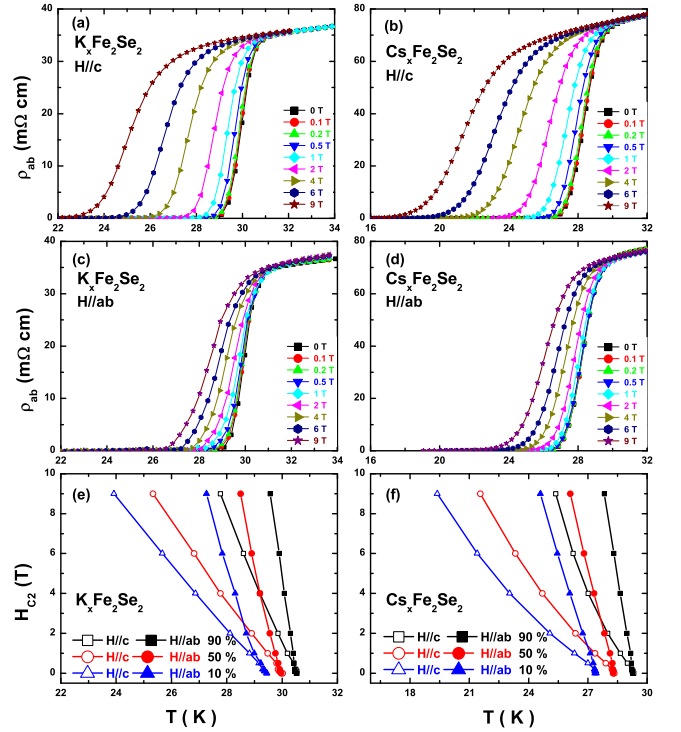


FIG. 4: (Color online) (a) and (c) show the temperature dependence of resistivity for  $K_{0.86}Fe_2Se_{1.82}$  crystal with the magnetic field parallel and perpendicular to the  $c$ -axis respectively; (b) and (d) show the temperature dependence of resistivity for  $Cs_{0.86}Fe_{1.66}Se_2$  crystal with the magnetic field parallel and perpendicular to the  $c$ -axis respectively; (e) and (f) show the temperature dependence of  $H_{c2}(T)$  for  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$ , respectively.

the data of  $H_{c2}(T)$  for the 90% resistivity drop, one can take  $[-(dH_{c2}^{ab}/dT)]_{T_c} = 9.86$  T/K,  $[-(dH_{c2}^c/dT)]_{T_c} = 3.17$  T/K and  $T_c = 30.5$  K. The  $H_{c2}(0)$  can be estimated to be 208 T and 67 T with the field parallel and perpendicular to the  $ab$ -plane respectively for  $K_{0.86}Fe_2Se_{1.82}$ , respectively. These values are a little larger than those in previous report. [16] For  $Cs_{0.86}Fe_{1.66}Se_2$  crystal, we take  $[-(dH_{c2}^{ab}/dT)]_{T_c} = 6.21$  T/K,  $[-(dH_{c2}^c/dT)]_{T_c} = 2.13$  T/K and  $T_c = 29.3$  K. The  $H_{c2}(0)$  is 126 T and 43 T with the field parallel and perpendicular to the  $ab$ -plane, respectively. They are much smaller than those of  $K_{0.86}Fe_2Se_{1.82}$  although their  $T_c$ s are close to each other. The anisotropy  $H_{c2}^{ab}(0)/H_{c2}^c(0)$  is about 3.1 and 2.9 for  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$ , respectively. This anisotropy value is larger than 1.70~1.86 in  $Ba_{0.60}K_{0.40}Fe_2As_2$  [21], but smaller than 4~6 in F-doped NdFeAsO [22].

Fig. 5 shows the magnetic susceptibility of  $Cs_{0.86}Fe_{1.66}Se_2$  with the magnetic field of 5 T applied parallel and perpendicular to the  $c$ -axis. The magnetic susceptibility decreases gradually with decreasing the temperature at high temperature. The susceptibility starts to go upward at around 120 K with the field perpendicular to the  $c$ -axis. While for the field

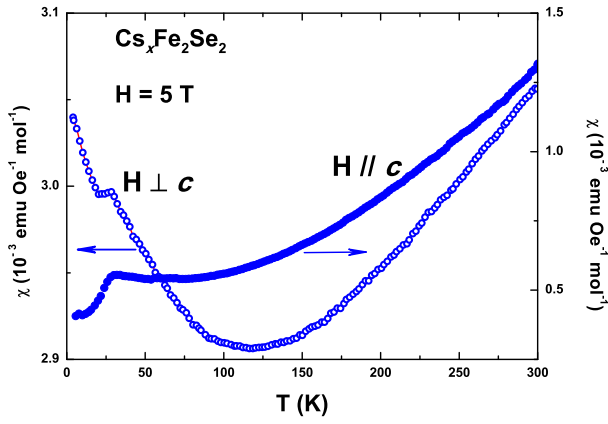


FIG. 5: (Color online) The magnetic susceptibility at 5 T for  $Cs_{0.86}Fe_{1.66}Se_2$  crystal with the magnetic field along and perpendicular to  $c$ -axis.

parallel to the  $c$ -axis, the susceptibility only shows very tiny upturn at around 70 K. The anomaly around 26 K is due to the transition of superconductivity. The susceptibility is larger as field is applied in  $ab$ -plane, which may suggest the spins lie within the plane. The peculiar magnetic behavior of  $Cs_xFe_2Se_2$  may be related to the deficiencies of Fe or the occurrence of the superconductivity. The decrease in susceptibility with decreasing temperature at high temperatures indicates there exists an antiferromagnetic coupling.

The occurrence of superconductivity could be related to such peculiar magnetic properties. The detailed magnetic structure requires further experiments.

In summary, we successfully grew the single crystals of K- and Cs-intercalated FeSe compounds.  $T_c^{\text{onset}}$  is 31 and 30 K for  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$ , respectively. The ZFC dc magnetic susceptibility indicates that the superconducting fraction is close to 100% for both types of crystal. The large  $H_{c2}$  observed in these materials is similar to the other iron-pnictide superconductors[5]. The anisotropy  $H_{c2}^{ab}(0)/H_{c2}^c(0)$  is around 3 for both the two materials. The normal state resistivity is very large compared with the other iron-based superconductors. Such large resistivity could arise from the Fe or Se vacancy in conducting FeSe layer. Very high electrical resistance in these superconducting compounds could challenge the theoretical scenario for the mechanism of superconductivity. Anisotropic peculiar magnetic behavior has been found in  $Cs_{0.86}Fe_{1.66}Se_2$  crystal. This may be related to the deficiencies of Fe. It should be addressed that their  $T_c$  is nearly the same although the resistivity behavior in  $K_{0.86}Fe_2Se_{1.82}$  and  $Cs_{0.86}Fe_{1.66}Se_2$  is quite different.

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